

## Thermal and Luminescent Properties of $M_2Zn(VO_3)_4$ ( $M = Rb, Cs$ )

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**Abstract**—We have developed processes for the synthesis of the  $Rb_2Zn(VO_3)_4$  and  $Cs_2Zn(VO_3)_4$  tetrametavanadates.  $Rb_2Zn(VO_3)_4$  has been prepared by solid-state reaction (350°C) between presynthesized  $RbVO_3$  and  $ZnV_2O_6$  powders, and  $Cs_2Zn(VO_3)_4$  has been prepared by the Pechini method (sol–gel process). Both metavanadates crystallize in monoclinic symmetry (sp. gr.  $P2_1/m$ ). Thermochemical characterization results demonstrate that the vanadates undergo complex transformations during heating to 450°C and subsequent cooling. As a result, the materials are in a nonequilibrium state at room temperature and consist of both the parent double metavanadates and their peritectic decomposition products. We believe that the formation of the structure of the  $M_2Zn(VO_3)_4$  compounds from their melts is a kinetically hindered process. These compounds are structurally stable only at temperatures below 369 ( $Rb_2Zn(VO_3)_4$ ) or 420°C ( $Cs_2Zn(VO_3)_4$ ). We have measured for the first time the diffuse reflectance and photoluminescence excitation spectra of the two tetrametavanadates in their emission range and their photoluminescence spectra at various excitation wavelengths and determined their chromaticity coordinates. Their X-ray luminescence and scintillation decay characteristics have been determined for the first time under pulsed electron beam excitation. The electron excitation dissipation processes in the cesium and rubidium compounds are shown to be similar. We discuss the origin of the emission bands in the mixed vanadates and their potential application areas.

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### INTRODUCTION

Vanadium compounds have long been used as efficient phosphors, laser gain media, and thermoluminescent dosimeters [1–5]. Nevertheless, the study of new individual compounds continues to receive a great deal of attention [2]. The poorly studied zinc-containing double vanadates with the general formula  $M_2Zn(VO_3)_4$ , where M is an alkali metal, constitute a new subclass of earlier synthesized vanadates [6–8].

The purpose of this work is to study the synthesis conditions, structure, and thermal and spectroscopic properties of the  $Rb_2Zn(VO_3)_4$  and  $Cs_2Zn(VO_3)_4$  tetrametavanadates, which contain rubidium and cesium spectrally active ions and the zinc cation, whose spectral activity in mixed metavanadates has not been studied previously. New vanadates have been tested for efficient red X-ray luminescence for medical applications.

### EXPERIMENTAL

**Sample preparation and characterization techniques.** The starting chemicals used in our preparations were  $V_2O_5$  (extrapure grade), ZnO (spectroscopically pure),  $Rb_2CO_3$  (reagent grade), and  $Cs_2CO_3$  (reagent grade).

$Rb_2Zn(VO_3)_4$  was synthesized in two steps. First, rubidium metavanadate was prepared through melting at 620°C (followed by cooling at a rate of 1°C/min in a platinum crucible) and zinc metavanadate was prepared by solid-state reaction (610°C, 60 h). In the second step, a mechanical mixture of  $RbVO_3$  and  $ZnV_2O_6$  powders was reacted at 350°C for 220 h. An attempt to prepare the double vanadate  $Rb_2Zn(VO_3)_4$  by the Pechini process was unsuccessful.

The  $Cs_2Zn(VO_3)_4$  metavanadate was synthesized by a sol–gel process. To a solution of an appropriate starting mixture in nitric acid was added citric acid and ethylene glycol in the molar ratio 1 : 3. The solution was boiled down to give first a dark piceous paste and then a polymeric precursor, which was heat-treated in air at 400°C for 200 h with intermediate grindings. The resultant powder was white in color, with a pink tinge.

The quality and purity of the samples were checked by X-ray diffraction (MAXima-X XRD-7000 diffractometer, Shimadzu, Japan). The X-ray diffraction characteristics of the double vanadates are presented in the table. The metavanadates crystallize in monoclinic symmetry (sp. gr.  $P2_1/m$ ). The unit-cell parameters of  $Rb_2Zn(VO_3)_4$  (refined by the Rietveld profile analysis method) are  $a = 19.2268(9)$  Å,  $b = 18.3868(9)$  Å,  $c = 9.0575(4)$  Å, and  $\beta = 91.848(3)^\circ$ , and those of  $Cs_2Zn(VO_3)_4$  are  $a = 20.196(1)$  Å,  $b = 19.360(1)$  Å,  $c = 9.412(1)$  Å, and  $\beta = 91.718(5)^\circ$ .

Interplanar spacings ( $d$ ) and relative intensities ( $I$ ) for the double vanadates

$I, \%$	$d, \text{Å}$	$I, \%$	$d, \text{Å}$	$I, \%$	$d, \text{Å}$	$I, \%$	$d, \text{Å}$	$I, \%$	$d, \text{Å}$
	$Rb_2Zn(VO_3)_4$	19	3.1367	9	2.0651		$Cs_2Zn(VO_3)_4$	5	2.4597
14	8.1068	56	3.1109	11	2.0247	5	7.8226	5	2.4341
13	7.8381	14	3.0855	7	2.0107	7	5.6437	5	2.4236
18	7.7841	10	3.0635	7	1.9945	14	4.1448	5	2.2984
10	5.7236	15	3.0204	7	1.9750	6	3.9515	5	2.1601
6	5.6759	25	2.9855	8	1.9641	10	3.9271	5	2.1560
6	5.4882	13	2.9167	22	1.9499	11	3.8257	5	2.1533
10	5.4109	28	2.8599	18	1.9429	12	3.8172	5	2.1209
16	5.2944	61	2.7541	10	1.9029	11	3.8065	5	2.1124
6	4.8245	16	2.7127	9	1.8584	10	3.7355	6	1.9884
5	4.7213	13	2.6543	8	1.8418	10	3.7258	9	1.9811
6	4.6225	11	2.6352	8	1.8049	11	3.5346	14	1.9777
6	4.4518	8	2.5978	9	1.7937	11	3.5219	7	1.9677
7	4.3928	13	2.5741	9	1.7717	100	3.4135	5	1.9638
7	4.3018	11	2.5656	8	1.7493	6	3.2875	5	1.9605
6	4.2589	17	2.5139	8	1.7420	13	3.2547	5	1.9061
9	4.1852	10	2.4839	9	1.7318	11	3.0734	7	1.7889
9	4.1461	10	2.4623	11	1.7215	16	3.0639	7	1.7868
13	4.0570	10	2.4469	13	1.7155	5	3.0220	9	1.7840
16	3.9966	11	2.3964	9	1.7102	5	2.8798	9	1.7821
11	3.8736	10	2.3836	8	1.6878	12	2.8292	9	1.7801
12	3.8028	8	2.3462	10	1.6839	40	2.7956	8	1.7783
20	3.7078	7	2.2866	11	1.6800	8	2.6141	6	1.7753
19	3.6671	8	2.2751	9	1.6763	9	2.6091	5	1.7706
23	3.5408	10	2.2145	8	1.6667	8	2.6047	5	1.7664
23	3.4766	9	2.1976	8	1.6611	8	2.5644	5	1.7622
31	3.4409	10	2.1370	12	1.6282	6	2.5578	8	1.7123
100	3.3409	9	2.1228	9	1.6255	7	2.5079	9	1.7095
22	3.2511	8	2.1087	8	1.6036	9	2.5033	6	1.7049
44	3.2104	10	2.0962			8	2.4937	5	1.7007

The vanadates were characterized by thermal analysis (SETARAM Setsys Evolution, France; temperature scan rate,  $10^\circ\text{C}/\text{min}$ ).

**Spectroscopic and luminescence properties.** The spectroscopic and luminescence properties of the zinc-containing metavanadates were studied at room temperature by measuring diffuse reflectance (DR), photoluminescence (PL), photoluminescence excitation (PLE), and X-ray luminescence (XRL) spectra and emission decay characteristics under pulsed electron beam excitation.

DR spectra were taken in the range 250–1100 nm on a PerkinElmer Lambda 35 spectrophotometer equipped with an integrating sphere for measurements on powder samples. The light sources used were deuterium and halogen lamps.

PLE (240–400 nm) and PL (400–800 nm) spectra were obtained on a PerkinElmer LS-55 spectrometer equipped with a fiber-optic accessory. PL was excited by a pulsed xenon lamp incorporated into the instrument. The emission was detected by a Hamamatsu R928 photomultiplier tube.

XRL spectra (210–780 nm) and emission decay characteristics were measured with an ASNI-ROSTT system (Institute of Physics and Technology, Yeltsin Federal University, Yekaterinburg) using a URS-01 X-ray generator (25–40 kV, 1.5–14 mA, W anode), MDR-2 monochromator (to separate out the spectral range of interest), and FEU-106 photomultiplier. Emission decay characteristics were determined under pulsed electron beam excitation. The experimental setup included an MIRA-2D electron gun (pulse

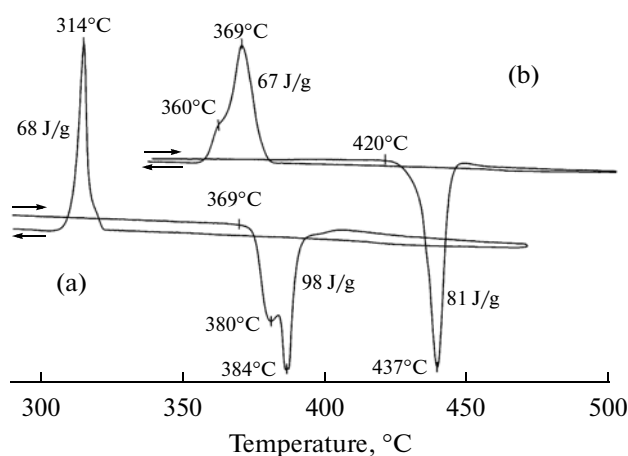


Fig. 1. Heating and cooling curves of (a)  $\text{Rb}_2\text{Zn}(\text{VO}_3)_4$  and (b)  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4$ .

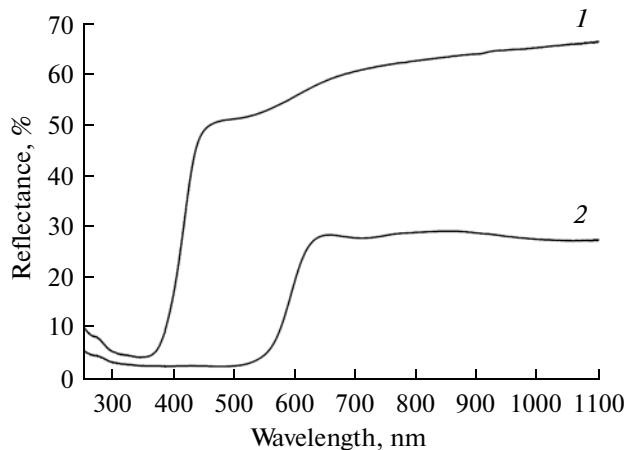


Fig. 2. DR spectra of (1)  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4$  and (2)  $\text{Rb}_2\text{Zn}(\text{VO}_3)_4$ .

duration  $\tau_p = 20$  ns, current density  $j = 150$  A/cm<sup>2</sup>, electron energy in the beam  $E = 150$  keV), MDR-2 monochromator, FEU-97 photomultiplier, and Tektronix TDS-5034B digital oscilloscope. The uncertainty in decay times  $\tau$  evaluated by a fitting procedure was  $\pm 0.05$   $\mu\text{s}$ . The overall uncertainty was within  $\pm 0.1$   $\mu\text{s}$ .

## RESULTS AND DISCUSSION

**Thermochemical characterization.** Thermochemical characterization results showed that heating and subsequent cooling led to complex transformations of our samples (Fig. 1). The melting onset temperature was  $369^\circ\text{C}$  in ( $\text{Rb}_2\text{Zn}(\text{VO}_3)_4$ ) and  $420^\circ\text{C}$  in  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4$ . The shape of the DTA heating and cooling curves and analysis of the samples cooled from  $450^\circ\text{C}$  to room temperature (furnace-cooled or quenched) indicate—in accord with X-ray diffraction data—the formation of nonequilibrium mixtures in

both cases, consisting predominantly of the parent double metavanadates and containing crystals of zinc pyrovanadate ( $\text{Zn}_2\text{V}_2\text{O}_7$ ) and low-melting-point rubidium vanadates in the case of the Rb system and crystals of zinc orthovanadate ( $\text{Zn}_3(\text{VO}_4)_2$ ) and low-melting-point cesium vanadates in the case of the Cs system. The nonequilibrium state and incongruent melting are also evidenced by comparison of the total enthalpies of the transformations (J/g in Fig. 1) that take place during heating and cooling of the metavanadates ( $\Sigma Q_{\text{heating}} > \Sigma Q_{\text{cooling}}$ ).

It is worth pointing out that changing the heating/cooling rate of our samples in the thermal analyzer (from 3 to  $10^\circ\text{C}/\text{min}$ ) and the report [6] that slow cooling of molten  $\text{K}_2\text{Zn}(\text{VO}_3)_4$  (chemical analog of the compounds under consideration) leads to crystallization of a phase-pure compound suggest that the formation of the structure of the  $\text{M}_2\text{Zn}(\text{VO}_3)_4$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ ) compounds is a kinetically hindered process. Thus, the compounds under investigation are structurally stable only at relatively low temperatures, and during their synthesis and heat treatment the phase composition of the samples should be checked.

**Optical properties.** The DR spectrum of the  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4$  metavanadate (Fig. 2, spectrum 1) has a flat, high-reflectance portion in the range 400–1100 nm. At wavelengths below 400 nm, the cesium zinc metavanadate effectively absorbs UV radiation. Near 520 nm, its absorption spectrum contains a weak absorption peak, responsible for the slightly pinkish tinge of the material. In the range 600–1100 nm, the reflectance of  $\text{Rb}_2\text{Zn}(\text{VO}_3)_4$  is half that of the cesium zinc metavanadate (Fig. 2, spectrum 2). Effective absorption in the rubidium zinc metavanadate occurs at wavelengths shorter than 590 nm, which shows up as a deep red color of the sample. The DR spectrum of this composition contains two weak, broad optical absorption bands centered at 710 and 1035 nm.

**PL.** The PLE spectra of  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4$  (Fig. 3) contain a broad band centered at 330 nm. A similar structure of PLE spectra was reported for the  $\text{M}_2\text{ZnV}_2\text{O}_7$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}$ ) zinc-containing pyrovanadates [2], which suggests that electronic excitation dissipation processes in these material are similar. Throughout the PL spectrum, the highest emission intensity was observed at an excitation wavelength of 240 nm (25–30% higher intensity in comparison with excitation at a wavelength of 330 nm). Excitation at wavelengths shorter than 240 nm (vacuum ultraviolet) requires further investigation.

The PL spectra of  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4$  at different excitation wavelengths (Fig. 3, curves 4, 5) consist of broad bands in the range 400–700 nm, centered around 535–540 nm. At an excitation wavelength of 330 nm, the PL spectrum of this vanadate contains a weak shoulder in the range 490–510 nm. On the whole, the PL spectrum of  $\text{Cs}_2\text{Zn}(\text{VO}_3)_4$  is dominated by green-yellow emission and is similar to those of other, earlier studied double cesium tetrametavanadates [2].

The excitation spectra of  $Rb_2Zn(VO_3)_4$  (Fig. 4, spectra 1, 2) contain a band at 330 nm, like the spectra of the cesium compound. A distinctive feature of the rubidium compound is that the luminescence yield of the green band at 510 nm is a relatively weak function of excitation wavelength in the spectral range 240–350 nm (variation by 15–20%).

The PL spectra of the double rubidium tetrametavanadate (Fig. 4, spectra 3, 4) consist of broad, composite bands with a well-defined maximum at 618 nm (peak emission range, 600–640 nm) and corresponds to an ideal red phosphor. In the range 500–570 nm, we observe a shoulder, like in the spectrum of  $Cs_2Zn(VO_3)_4$ .

As seen in Fig. 4,  $Rb_2Zn(VO_3)_4$ -based phosphors have an almost constant PL yield (to within 15–20%) at excitation wavelengths from 240 to 350 nm, which may be of interest in designing compact devices for monitoring spectral characteristics of UV sources operating in combination with PIN photodiodes, because these latter are known to have the highest sensitivity in the red spectral region. A sodium-salicylate-based phosphor commonly used for this purpose has blue emission, but PIN photodiodes have low sensitivity in the blue.

From the measured PL spectra of the vanadates, we evaluated their chromaticity coordinates: (0.34, 0.47) for  $Cs_2Zn(VO_3)_4$  and (0.47, 0.43) for  $Rb_2Zn(VO_3)_4$ .

**XRL.** The XRL spectra of the  $Rb_2Zn(VO_3)_4$  and  $Cs_2Zn(VO_3)_4$  vanadates are presented in Fig. 5 in comparison with the XRL spectrum of  $ZnV_2O_6$ . The XRL spectrum of the cesium compound is dominated by a band at 540 nm, whereas the XRL spectrum of the rubidium compound consists of two bands, at 460 and 606 nm.  $ZnV_2O_6$ , whose XRL intensity is a factor of 10–15 lower than the XRL intensity of the double cesium and rubidium metavanadates under consideration, has an XRL band in the blue spectral region, at 420 nm. The observed shape of the XRL spectrum of  $Rb_2Zn(VO_3)_4$  (redshifted) seems to be due to specific features of light absorption by neutral oxygen vacancies in this compound (Fig. 2, spectrum 2), by analogy with the  $M_2Sr(VO_3)_4$  ( $M = Na, K, Rb, Cs$ ) strontium metavanadates [2]. This also accounts for the shape of the PL spectrum of this compound (Fig. 4, spectra 3, 4).

One purpose of this study was to find X-ray luminescence sensitizers that would ensure malignant cell destruction (eradication) by transferring surrounding oxygen molecules to an active singlet state and to create sensitizers capable of operating in conjunction with a Fotosens-type medication for selective photodynamic therapy. In this respect, both phosphors under investigation are of interest:  $Cs_2Zn(VO_3)_4$ , with bright XRL in the range 500–640 nm, and  $Rb_2Zn(VO_3)_4$ , with XRL in the range 570–650 nm. The emission spectrum of  $Cs_2Zn(VO_3)_4$  fits well with spectral characteristics of Fotosens [9], so this vanadate appears potentially attractive for use as an X-ray phosphor in photodynamic oncological therapy.

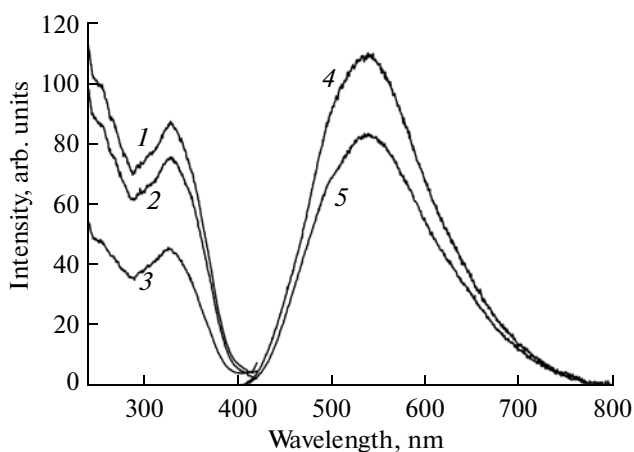


Fig. 3. (1–3) PLE and (4, 5) PL spectra of  $Cs_2Zn(VO_3)_4$ :  $\lambda_{lum} =$  (1) 590, (2) 640, (3) 470, (4) 240, and (5) 330 nm.

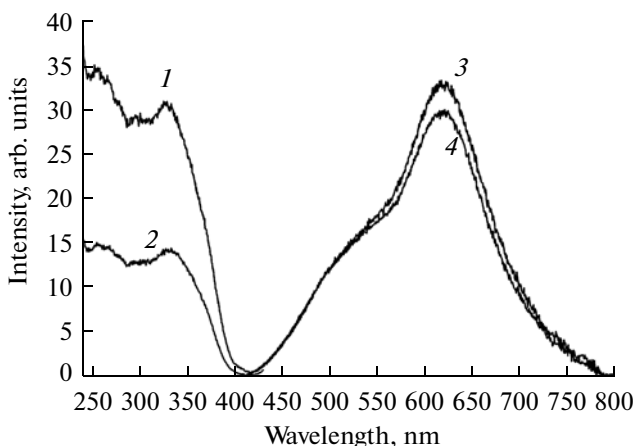


Fig. 4. PLE (1, 2) and (3, 4) PL spectra of  $Rb_2Zn(VO_3)_4$ :  $\lambda_{lum} =$  (1) 620, (2) 510, (3) 330, and (4) 256 nm.

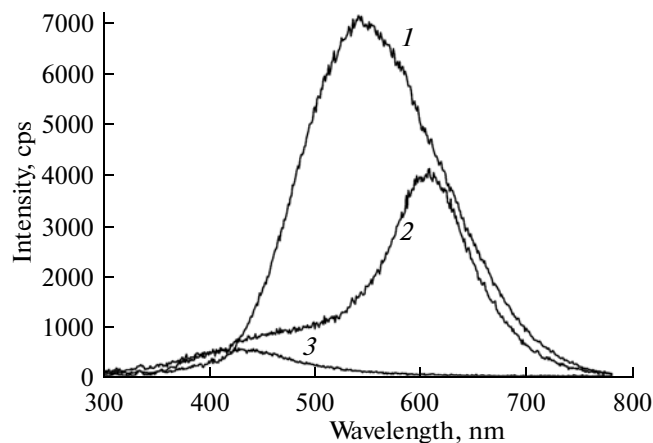


Fig. 5. XRL spectra of (1)  $Cs_2Zn(VO_3)_4$ , (2)  $Rb_2Zn(VO_3)_4$ , and (3)  $ZnV_2O_6$ .

A search for potential X-ray luminescence photosensitizers among vanadates is prompted by the known photocatalytic properties of vanadates [2, 11, 12], in which absorbed energy dissipation is accompanied by the generation of active  $O^-$  centers. When such centers surround a tumor and are in an excited singlet state, they contribute to the destruction of tumor cells [9, 10].

**Luminescence decay characteristics.** Our experimental data on the luminescence decay time in different spectral ranges lead us to conclude that the duration of the scintillation induced by a pulsed electron beam is similar to that in other vanadates [1, 2]: 34.4  $\mu$ s (540-nm band) in  $Cs_2Zn(VO_3)_4$  and 11.2 (603-nm band) and 1.58  $\mu$ s (460-nm band) in  $Rb_2Zn(VO_3)_4$ .

### CONCLUSIONS

We have developed a process for the synthesis of the double tetrametavanadates  $Rb_2Zn(VO_3)_4$  and  $Cs_2Zn(VO_3)_4$  and investigated their thermochemical, optical, photoluminescent, X-ray luminescent, and luminescence decay properties. We have assessed their spectroscopic and decay characteristics and chromaticity coordinates.

These vanadates are of interest for both scientific and technological applications as phosphors with specific spectral properties. In particular, a  $Rb_2Zn(VO_3)_4$ -based phosphor with a constant PL yield in the range 240–350 nm is of interest in designing compact PIN photodiode devices for monitoring the intensity of UV sources. A  $Cs_2Zn(VO_3)_4$ -based phosphor appears potentially attractive as an X-ray luminescence photosensitizer in photodynamic oncological therapy, because it offers a high XRL yield in the range 570–650 nm and because absorbed energy dissipation in it is accompanied by the generation of active  $O^-$  centers.

### ACKNOWLEDGMENTS

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